

## PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO  
 PALLADIUM CATALYSIS

(71) We, JOHNSON, MATTHEY & CO., LIMITED, a British Company, of 43 Hatton Garden, London, EC1N 8EE, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalysts and more particularly to palladium catalysts exhibiting enhanced activity.

Palladium catalysts consisting of metallic palladium deposited within solid porous particulate supports must necessarily possess a lower specific activity per unit area of deposited metal. It is an object of the present invention to at least in part overcome this deficiency.

According to one aspect of the present invention a process for the preparation of a supported palladium catalyst comprises the vapour deposition of a compound of palladium onto a solid porous particulate support in which the said support is at a temperature above the decomposition temperature of the said compound of palladium.

According to another aspect of the present invention a catalyst comprises metallic palladium deposited on a porous particulate solid in such a way that the metallic palladium remains on the outside of the particle and is deposited only within the pore mouths of those pores having a diameter greater than 50 Å units.

A preferred compound of palladium is bisacetylacetonato palladium (II) and a preferred support is charcoal in powder form. In the process of the present invention an evacuated flask containing the compound of palladium is heated such that the said compound distils and sublimes onto the surface of the powder carbon which is preferably kept agitated by rotation in a tumbler flask containing the compound of palladium. Preferably the carbon is simultaneously heated to a temperature above the decomposition point of the compound of palladium. Palladium metal is found to deposit on the external surfaces of the carbon particles and only in the mouths of those pores which have a diameter greater than approximately 50 Å units. Substantially no palladium is found to deposit in the mouths of pores having a diameter less than 50 Å units wide.

Pore lengths are commonly ten times their diameter at the opening (referred to herein as the "mouth"). Thus the large pore running the length of Figure 2 is approximately 1000 Å in length and about 1000 Å in diameter. The lining, throughout its length, of black specks indicates the presence of metallic palladium along the whole length of the pore.

Pores with mouths having a diameter within the range of 50—500 Å units are found to have metallic palladium deposited within them along the lining of the pore walls down to a depth within the range 100—500 Å units.

Such catalysts are useful in the catalytic hydrogenation of edible oils of animal and vegetable origin so as to improve their qualities without at the same time impairing the nutritional value or edibility of the oil.

Catalysts according to the present invention are eminently suitable for use in the hydrogenation process described in British Patent Application No. 5385/76 dated 11th February 1976; British Patent Application No. 5385/76 (Serial No. 1,578,122) is concerned with the hydrogenation of the trienoic unsaturated forms of the fatty acid present within animal and vegetable oils to the dienoic unsaturated forms. Certain performance details of a Pd/C catalyst according to the present invention are given in Application No. 5385/76 which is concerned with this

reaction. Such catalysts have considerable advantages as regards the much lower rate of cis-trans isomerisation, doubled bond migration and unwanted saturation of double bonds.

Suitable supports which may be used are porous carbon, alumina, kieselguhr and the various forms of porous silica gel which are available as catalyst supports.

The resulting structure of the catalyst is confirmed by electron micrograph (see photomicrographs in Figures 2 and 3) and ESCA (Electron Spectroscopy for chemical analysis) which indicate that virtually all of the palladium in metallic form is either on the outside of the particle or present in the mouths of those pores having a diameter greater than 50 Å units.

Figures for the specific activity per square metre of surface area of metal of a catalyst according to the invention compared with a conventionally prepared palladium on carbon catalyst are given in Example 3.

ESCA measurements of both types of catalyst confirm the presence of the palladium at or near the surface of the support in only the catalyst according to the present invention. In ESCA measurements it is known that the quantity of element is proportional to the area under the peak. Whereas the area for the carbon peaks remains the same for both types of catalyst, the palladium peaks (as Pd produces a doublet) are much higher for catalysts according to the present invention. As it is known that electron release producing ESCA readings only result from the top layer of the structure (i.e. from the surface down to 100 Å maximum) the increased Pd reading is indicative of a much greater metallic palladium deposit at the surface of the structure.

#### Example 1

8.8 gms of bisacetylacetonato palladium II equivalent to 2.5 gms palladium metal is placed in vessel, 1, of the apparatus illustrated in Figure 1. Into vessel, 2, is placed 50 gms charcoal, 3, previously dried at 105°C in an air oven. The apparatus is assembled and connected to a vacuum pump, 4, via a liquid nitrogen cold trap.

Vessel 2 is surrounded by a thermostatically controlled electrical air oven, 5; vessel 1 is immersed partially in a bath of silicone oil, 6, whose temperature is controlled thermostatically.

The vacuum pump is started and allowed to attain a vacuum of 0.1 mm or better. The air oven surrounding vessel 2 is heated slowly to 300°C while its contents are tumbled at 40 rpm to allow volatile materials absorbed on the charcoal to be removed. When the temperature has attained 300°C, the thermostat on the silicone oil bath surrounding vessel 1, is set to 160—165°C and switched on. After 2 hours when all of the bis acetylacetonato palladium (II) has been volatilised, the silicone oil bath and the air oven are switched off and allowed to cool. Once cool, nitrogen is admitted to the apparatus until the pressure attains atmospheric pressure. The apparatus is then disconnected and the catalyst unloaded.

The catalyst after mounting in an epoxy resin medium was sectioned on a diamond knife microtome to give slices approximately 500 Å in thickness and examined in an AEI EM6G electron microscope. The electron micrograph shown in Figure 2 was obtained.

A large pore containing metallic palladium throughout its length can be seen together with cross-sections of some small pores having no metallic deposit. The figure is purely for the purposes of illustration of catalyst structures according to the present invention.

#### Example 2 (Comparative)

A catalyst was prepared on the same charcoal as example 1, by absorbing chloropalladous acid from aqueous solution, reducing the palladium compound to the metal with alkaline formaldehyde, and drying the catalyst, after washing to remove alkali, at 105°C.

Examination of the catalyst in an AEI EM6G electron micrograph showed a uniform distribution of metal throughout the particles as in Figure 3. Figure 3 has higher magnification and pores are visible, but it can be seen that the metallic deposit is not confined, but is distributed throughout the support.

#### Example 3

The activity of the catalysts prepared in Examples 1 and 2 were measured by hydrogenating (i) 20 mls 6% nitrobenzene in methanol and (ii) 20 mls 32% oleic acid

in methanol with 0.1 gms catalyst in a shaken reactor. The activity of the catalyst was calculated by noting the rate at which hydrogen was absorbed from a gas burette system constantly adjusted to maintain the gas pressure within the system at 1 atmosphere. The temperature of reaction vessel was held at 30°C during the hydrogenation by a thermostatically controlled water bath.

The activity of the two catalysts of examples 1 and 2 are shown in Table 1 together with their metal areas measured by carbon monoxide chemisorption.

TABLE 1

	Activity Nitrobenzene	mls/min/ 0.1 g cat Oleic Acid	Metal Area m <sup>2</sup> g <sup>-1</sup>
Catalyst of Example 1	770	32.5	14
Catalyst of Example 2	25	11.5	52

Table 2 shows the specific activity per unit metal area (mls H<sub>2</sub> taken up per m<sup>2</sup> metal area).

TABLE 2  
Specific Activity

	Nitrobenzene	Oleic Acid
Catalyst of Example 1	550	23.2
Catalyst of Example 2	4.8	2.2

As can be seen from Table 2 the catalyst prepared by example 1 has by far the higher specific activity of the two examples in both catalytic reactions and in consequence the palladium metal must be deposited more closely to the support surface in example 1 than in example 2, a fact borne out by the electron micrographs of Figures 2 and 3 and by ESCA measurement.

## WHAT WE CLAIM IS:—

1. A process for the preparation of a supported palladium catalyst comprising the vapour deposition of a compound of palladium onto a solid porous particulate support and during deposition the support is maintained at a temperature above the decomposition temperature of the compound of palladium.

2. A process according to Claim 1 wherein metallic palladium from the said compound is deposited on the external surface of the particles of the support and within those pores having a diameter greater than 50 Å units.

3. A process according to Claim 1 or Claim 2 wherein the solid porous particulate support is made from porous carbon, charcoal, alumina, kieselguhr or porous silica gel.

4. A process according to Claims 1, 2 or 3 wherein the compound of palladium is bisacetylacetonato palladium (II).

5. A process according to Claim 1 wherein the support is maintained at a temperature of the order of 300°C and wherein the support is agitated prior to and during deposition thereon of the said compound.

6. A process according to Claim 5 wherein prior to deposition the said compound and the said support are contained in separate containers and the compound is heated prior to transference into the container containing the support.

7. A process according to Claim 6 wherein transference and deposition is accomplished under vacuum.

8. A catalyst comprising metallic palladium deposited on a porous particulate solid in such a way that the metallic palladium remains on the outside of the particle and is deposited only within the pore mouths of those pores having a diameter greater than 50 Å units.

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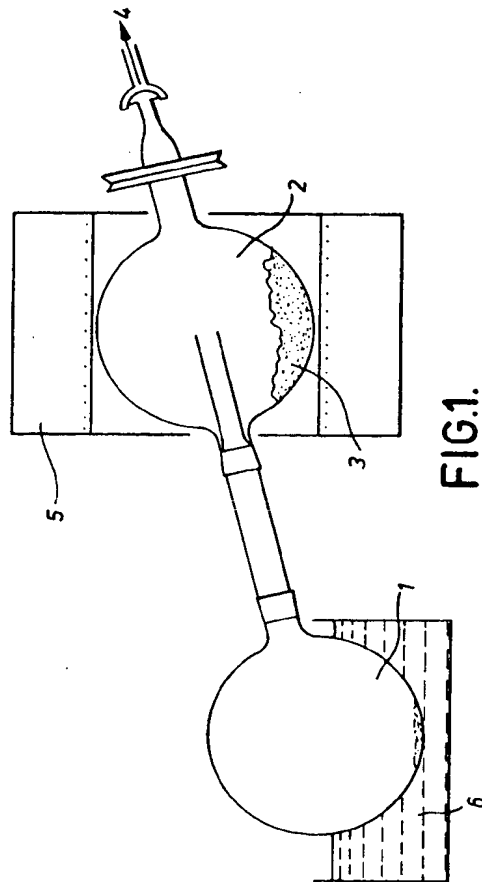
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COMPLETE SPECIFICATION

3 SHEETS

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Sheet 1



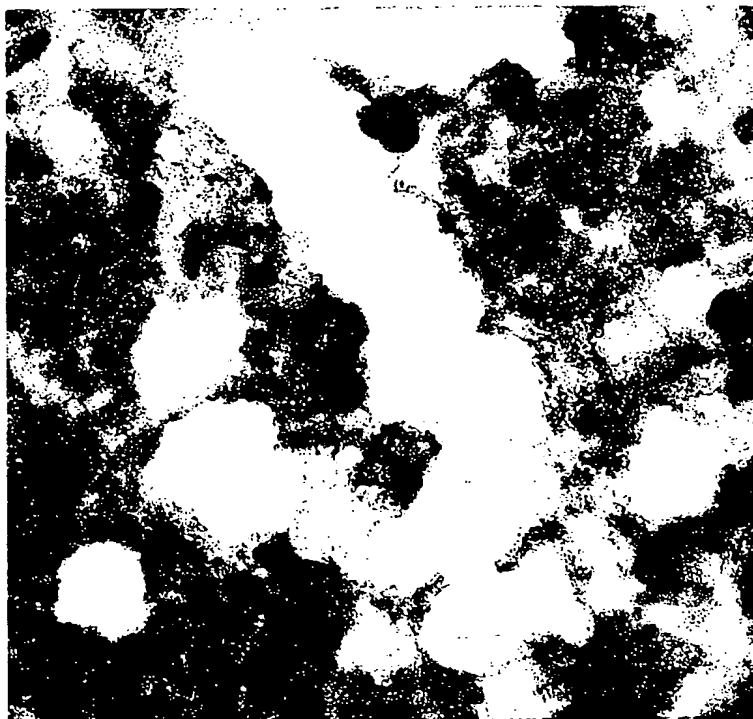
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COMPLETE SPECIFICATION

3 SHEETS

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Sheet 2

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5% Pd/CHARCOAL  
MAGNIFICATION X 150,000

*FIG.2.*

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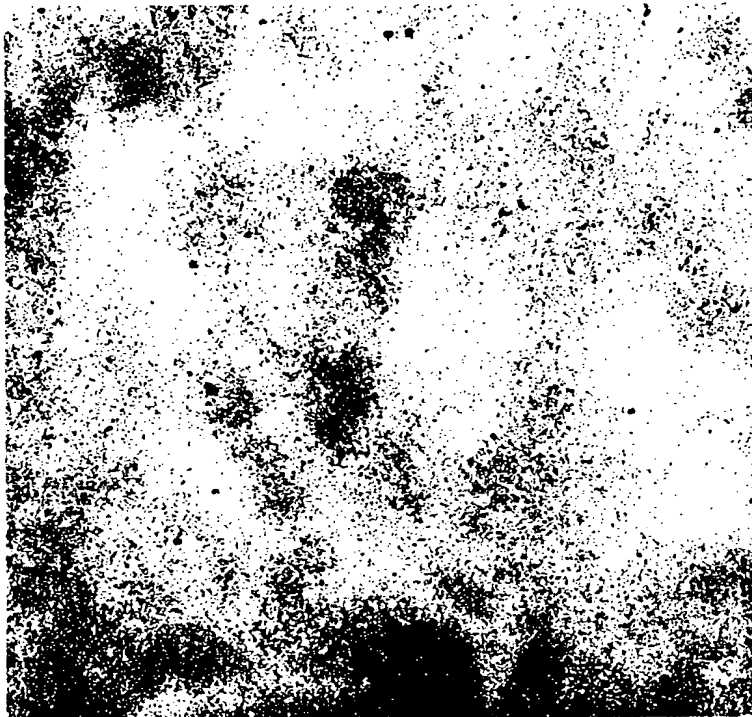
COMPLETE SPECIFICATION

3 SHEETS

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Sheet 3

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5% Pd/CHARCOAL  
MAGNIFICATION X 250000  
FIG.3.